



**John L. Margrave**

1924–2003

BIOGRAPHICAL

*Memoirs*

*A Biographical Memoir by  
James L. Kinsey*

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NATIONAL ACADEMY OF SCIENCES

# JOHN LEE MARGRAVE

April 13, 1924–December 18, 2003

Elected to the NAS, 1974

John Lee Margrave was born April 13, 1924, in Kansas City, Kansas, to Orville F. and Bernice June Hamilton Margrave. In school he was an outstanding student and an avid participant in extracurricular activities. He achieved the rank of Eagle Scout, edited his high school's newspaper, played on the baseball team, and was a star on the tennis team. He took violin lessons and derived much joy from playing the violin throughout his adult years.

John continued to live in Kansas City through his high school graduation. He entered the University of Kansas at Lawrence under a Summerfield Scholarship, but his education was interrupted by World War II. He enlisted in the Army Signal Corps in 1941 and trained at Camp Callen in San Diego, becoming an expert marksman. He served on active duty from 1943 through 1946, during part of which time he was stationed at Ulm, Germany, where he was in charge of a telephone repeat station. He learned German there and took correspondence courses to further his studies. Later, he transferred from the Signal Corps to the Chemical Corps.



A handwritten signature in dark ink, which appears to read "J. Margrave". The signature is written in a cursive style.

By James L. Kinsey

Upon leaving the army, John returned to the University of Kansas, where he was a Summerfield Scholar and a Slosson Fellow. He received a B.S. in engineering physics in 1948. During his undergraduate years, however, he developed a deep and enduring passion for chemistry that persisted to the end of his life. Immediately after receiving his B.S. John enrolled in the graduate program of the university's chemistry department. He was the first graduate advisee of Professor Paul W. Gilles, who himself had been the first graduate student of Leo Brewer. John would later encounter Brewer at the University of California at Berkeley. John's work in Gilles's laboratory—partly fluorine chemistry and partly high-temperature/high-pressure chemistry—was a preview of his later career, much of which was devoted to "chemistry under extreme conditions." Evidently his experimental skills were already exceptional: He earned his Ph.D. degree in only two years,

including having written a 300-page dissertation. In the same year he got his doctorate, he married Mary Lou Davis, the daughter of a prominent Kansas family.

### **An academic career begins**

In 1951 John went to UC Berkeley to be an Atomic Energy Commission postdoctoral fellow in the laboratory of Leo Brewer. During his time at Berkeley, he published papers with W. A. Klemperer, K. Wieland, and D. Templeton in addition to Brewer. Although they did not collaborate at the time, John also met and befriended Kenneth Pitzer, who would later be instrumental in bringing him to Rice University.

In the fall of 1952, at the end of his AEC fellowship, John accepted an appointment as an instructor in the chemistry department at the University of Wisconsin-Madison. There he began to set up a world-class laboratory for research in high-temperature chemistry. This was no trivial task, because the systems usually involved multiple equilibria, with multiple participating chemical species. To do definitive work required bringing a wide collection of techniques to bear on each problem: X-ray powder diffraction; IR, visible, and UV spectroscopy; mass spectrometry; vapor density measurements; comparison of flow, effusion, and static vapor pressure measurements, etc. Notwithstanding these formidable requirements, a stream of papers began to originate from John's Madison laboratory within his first couple of years there. Shortly this stream became a torrent.

A partial list of areas John touched upon in these studies includes metal nitrides, metal oxides, metal hydroxides, boron compounds, hydrides, alkali metal oxides, inorganic nitrides, carbides and borides, platinum metals, silicon compounds, and fluorine compounds. His earliest studies mainly focused on identifying the participating chemical species, many of which were previously unknown. As the program matured, it expanded to include determination of thermodynamic properties such as standard enthalpies and entropies of formation from the elements, equilibrium constants, and vapor pressures as functions of temperature.

Much of this high-temperature chemistry involved the fluorine bomb calorimeter, which John perfected in a collaboration extending over many years with Dr. Ward Hubbard of Argonne National Laboratory. Fluorine bomb calorimetry provided a way of obtaining thermochemical data in cases where the results of the usual oxygen bomb calorimetry might be poorly defined. The fluorine compounds were mostly gaseous and better characterized.

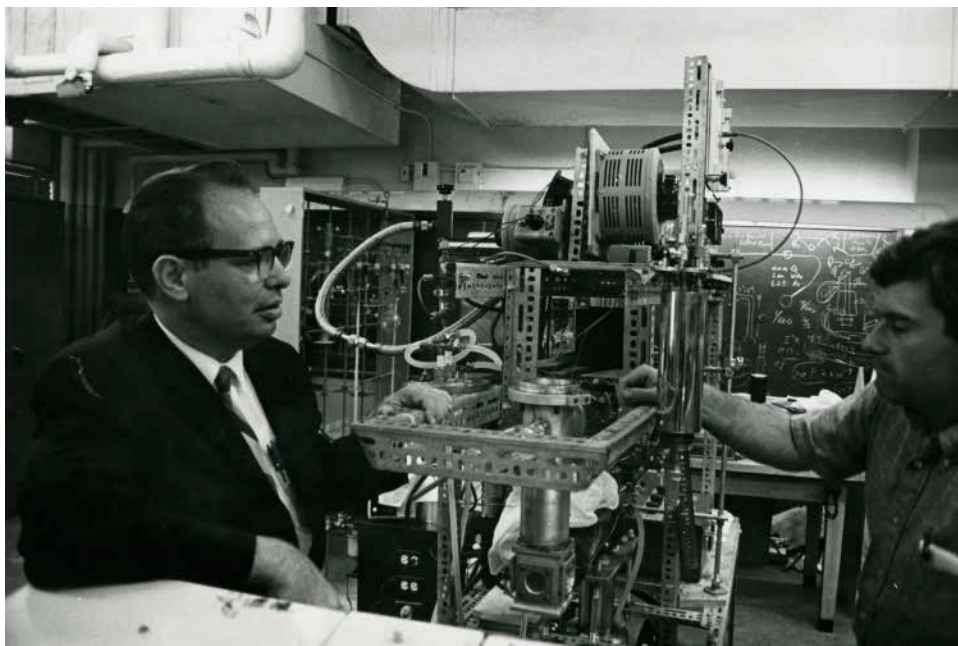
John's initial laboratory at Madison also included work on the chemistry and thermochemistry of elemental fluorine—an outgrowth of his Ph.D. dissertation research. The ability to fluorinate would continue to be part of his toolkit for the remainder of his life.

In 1963 John accepted an offer to join the chemistry faculty at Rice, where the university president was his friend Kenneth Pitzer from Berkeley days. At Rice he maintained the pace of research that his Madison career had established. His continued applications of fluorine chemistry focused on discovery and characterization of new species. His research group developed methods for direct fluorination to make  $CF_x$  species. One of the most prominent applications was the fluorination of graphite to  $C_1F_1$  graphite (“white graphite”), which is used as a source of F in LiF batteries. Various companies had tried to make this substance but had failed, even though it is thermally stable.  $C_1F_1$  was also considered as a candidate for an additive lubricant in motor oils, but it proved too expensive for widespread use. The solid fluorocarbon lubricant “CFX” won John and his research group an R&D100 Award in 1970. It has proved to be one of the best high-temperature lubricants for oxidizing or corrosive environments.

John and his graduate student Richard Lagow developed fluoro coatings for many things, ranging from surgical gloves to Barbie Dolls. The two worked out a method known as the La Mar (after the first syllables of their names) process for fluorocoating materials by direct reaction of  $F_2$  with hydrocarbons.

Beginning shortly before John's departure from Wisconsin and continuing in great force at Rice was a 35-paper series of investigations called “Mass Spectrometric Studies at High Temperatures.” In this work and related papers he reported properties of approximately 100 high-temperature metal fluoride species. Most of these species were not previously known. Using mass spectrometry as the primary analytical tool, John and his teams obtained properties such as sublimation pressures, standard enthalpies of formation, dissociation energies, heats of sublimation, vapor equilibria, reactivities, stabilities, and ionization potentials.

John was always on the alert for new techniques in the furtherance of “chemistry under extreme conditions,” and he was so intrigued with the advances of Dr. Tracy Hall in producing artificial diamonds at ultra-high pressures that he spent part of a Guggenheim Fellowship in 1961 in Dr. Hall's laboratory, which had by that time located to Brigham Young University.



Margrave, left, and another man, examining a piece of machinery, 1965.

(Photo courtesy Rice University, licensed under a Creative Commons Attribution 3.0 Unported license.)

John didn't get a chance to explore the high-pressure regime in the laboratory until several years later (1967-1972), after his move to Rice. His graduate student C.-H. Chang constructed opposed anvil and tetrahedral anvil devices, which he used to study thermal decompositions at high temperatures and high pressures, syntheses of new cubic metaborates and syntheses, and properties of group III metaborates. In further studies John focused on syntheses of high-pressure  $\text{LiMO}_2$  and reactions of  $\text{Li}_2\text{O}_2$ .

Starting in the mid-1960s and continuing for about a dozen years, John's laboratory carried out extensive investigations into the chemistry of divalent compounds of group IVb elements. A broad range of species was investigated— $\text{SiO}_2$ ,  $\text{SiS}_2$ ,  $\text{GeF}_2$ ,  $\text{GeCl}_2$ ,  $\text{GeO}_2$ ,  $\text{GeS}_2$ ,  $\text{SnF}_2$ ,  $\text{PbF}_2$ , etc. These carbene analogs were of interest because they were probable intermediates in a wide variety of reactions and could provide routes to the synthesis of exotic species. The fluorides were of special interest to John for their unusual stability: Whereas the half life of carbene itself ( $\text{CH}_2$ ) is in the microsecond range,  $\text{CF}_2$

has a half-life in the gas phase of around 1 second. Hence most of his work in this area centered on  $\text{CF}_2$  and  $\text{SiF}_2$ —especially the latter.

Reports of observations of  $\text{SiF}_2$  had appeared in the literature prior to John's investigations, but most of these likely involved the polymeric form  $(\text{SiF}_2)_x$  and not the monomer.  $\text{SiF}_2$  was prepared via a straightforward reaction of silica with  $\text{SiF}_4$  at high temperature and low pressure. If the reactants and products were kept in contact with each other, the primary product was the polymer, but monomeric  $\text{SiF}_2$  was easily obtained by pumping the system during the reaction. The polymer is pyrophoric and highly reactive. Fluorine bomb calorimetry was used to determine the Si-Si bond strength in  $(\text{SiF}_2)_x$  and various spectroscopic means were employed to determine its structure.

Monomeric  $\text{SiF}_2$  obtained in the pumped-off material turned out to be surprisingly stable. It had a half life of about 150 seconds. Moreover, the chief cause of its disappearance was reaction at the vessel walls, not spontaneous decomposition. This monomer proved extremely tractable and enabled John and his team to make a number of physical measurements, such as UHV spectroscopy, microwave spectroscopy, and infrared spectroscopy. From these investigations they determined the bond angle and bond length, along with the molecular dipole moment and standard enthalpy of formation from the elements. They were also able to do extensive studies on the reactions and kinetics of silicon difluoride, which is a highly reactive species with both inorganic and organic molecules. And they used  $\text{SiF}_2$  as a reagent for preparation of a rich set of new substances.

John and his researchers pioneered a new technique, levitation calorimetry, for studying the high-temperature properties of liquid metals. This method employed electromagnetic fields to float samples in midair without the need for a container. They then applied heat inductively to the samples, allowing them to investigate thermodynamic and transport properties of a number of high-melting metals, such as niobium, zirconium, cobalt, palladium, titanium, and silver. The heat capacities and enthalpies of fusion of these elements would have been difficult if not impossible to obtain by other methods.

Among the equipment that had moved to Rice with Pitzer's laboratory was an apparatus for matrix isolation spectroscopy. In the mid-1960s, with Pitzer's approval, John and his postdoctoral associate Robert Hauge started to use this apparatus. This was the beginning of an extremely fruitful line of inquiry by John's group and the beginning of a long and productive collaboration. Hauge and John would continue to work together for the rest of John's life, with Hauge eventually becoming a member of the Rice University research

faculty and an independent investigator in his own right. After using Pitzer's apparatus for a few months, Hauge and John built a new and improved version.

The matrix isolation technique proved to be an ideal vehicle for advancing John's program on high-temperature species. In its original form, a dilute mixture of unstable and reactive molecules in a rare-gas solvent is sprayed onto a rotating drum maintained at a low temperature, typically  $\sim 15\text{K}$ . The rare gas (usually argon) forms a glassy matrix that traps and stabilizes the otherwise transient species. This accomplishes two things: The reactive molecules are effectively immobilized so that they cannot interact with each other or with any but the nearest solvent molecules, and they are cooled to the temperature of the matrix, thereby slowing unimolecular transformations. These properties permitted the detailed spectroscopic characterization of the many new and exotic species that John's team discovered. The main spectroscopic technique was infrared spectroscopy (and its Fourier-transform variant). Electron spin resonance spectroscopy and visible and ultraviolet spectroscopy were also used in many of the studies.

These investigations into high-temperature species produced a wealth of data on an enormous number of previously uncharacterized species, including (but not limited to) rare-earth chlorides and fluorides and main-group metals. Spectroscopic data yielded molecular parameters, such as bond lengths, bond angles, determination of planarity or lack of it, and other structural information. These data, in turn, could feed calculations of thermodynamic properties at high temperatures. Nowadays researchers might turn to various existing *ab initio* quantum chemistry packages to provide such information, but at the time there was no substitute for actual measurements.

John's matrix studies progressed into investigations of reactivity and kinetics, initially in argon matrices. The cold surface would be bombarded with sprays of two reactive species, such as a metal and water or a metal and a small hydrocarbon. Often this resulted in a simple metal-complex that produced minor but informative changes in the water molecule's spectrum, providing the researchers with insight into the degree of complexation of association of water with various metals. John's reactivity studies started with  $\text{H}_2\text{O}$  and moved on to simple hydrocarbons—methane, ethane, ethylene, acetylene. Vibrational frequencies of previously unknown species appeared:  $\text{HFeCH}_3$ ,  $\text{Fe}=\text{CH}_2$ ,  $\text{Fe}\equiv\text{CH}$ . Matrix-trapped metals could also be electronically excited by appropriate light sources. This led to studies of the chemistry of the excited species.

In one set of these studies, matrices of pure  $\text{F}_2$  (hardly inert!) were bombarded with ethane, ethylene, acetylene, and other small hydrocarbons. All these reactants would go

into the  $F_2$  matrix intact, then react there. Chemical transformations of resulting species could be monitored by following the IR spectra. A seminal achievement involved the first C-H activation of methane by a transition metal. The researchers found photo-excited cobalt atoms to insert into the carbon-hydrogen bonds of methane to yield  $CH_3CoH$ . Photolysis of  $CH_3CoH$  using 400 nm light led to extrusion of the metal and the formation of the spectroscopically detectable  $Co(CH_4)$  sigma-complex, which was shown to have  $C_{3v}$  symmetry. Photolysis of this complex using a UV source regenerated the insertion product  $CH_3CoH$ . This same species could be microsynthesized by co-condensing the metal with  $CH_2N_2$ ,  $H_2$  and argon at 11 K. The product was characterized using FTIR spectroscopy. Vibrational frequencies of other previously unknown species were also seen, including  $Fe=CH_2$  and  $Fe\equiv CH$ .

One of the earliest examples of photochemistry induced by vibrational excitation was obtained in John's laboratory by irradiating  $C_2H_2$  that was trapped in a fluorine matrix, using infrared light from the light source of an IR spectrometer. The IR light was coarsely wavelength selected with filters. Reaction occurred when the band of wavelengths passing through the filter corresponded approximately to vibrational frequencies of  $C_2H_2$ . This strongly suggested the possibility of bond-specific activation of a chemical reaction. No clear experimental example of this phenomenon was known at the time, so the result, when John et al. published it, was controversial. Fortunately, it was later confirmed by IR laser experiments in another laboratory.

An offshoot of this line of work was the design and construction of a super matrix isolation apparatus (Cryolink) with laser desorption evaporation and mass spectrometric detection. This earned John and his team a second R&D100 Award in 1986.

In the early 1990s, John began a collaboration with M. P. D'Evelyn, R. H. Hauge, and others on the chemical vapor deposition (CVD) of diamond films. Isotopic studies using  $^{12}C$  and  $^{13}C$  indicated the importance of the  $CH_3$  radical in the deposition process and allowed determination of the fundamental mechanisms of growth. Halogen-assisted CVD was explored and exploited. A later collaboration with V. N. Khabashesku and others dealt with functionalization of nanoscale diamond powders.

In 1985 John had a front-row seat at the discovery of  $C_{60}$  and the fullerenes by his Rice colleagues Robert Curl and Richard Smalley and their visiting colleague Harold Kroto, which was later to earn them the 1996 Nobel Prize in Chemistry. John was quick to realize the potential for new discoveries in basic chemistry that were laid open by this new form of carbon. He almost immediately entered into a collaboration with Smalley,



along with W. E. Billups, Hauge, and others, on fluorine chemistry of  $C_{60}$  and carbon nanotubes. They found it possible to fluorinate the outside of fullerenes and nanotubes. Fluorine turned out to be one of the few reactants that could reach every nanotube in a bundle, and therefore it provided a good start for further chemistry. Subsequent reaction with Li-alkyl, for example, allowed alkylation of fullerenes and single-walled nanotubes, which gave solubility to these species. Fluorination of nanotubes followed by pyrolysis led to a method for cutting the nanotubes. This technique led to a third R&D100 Award.

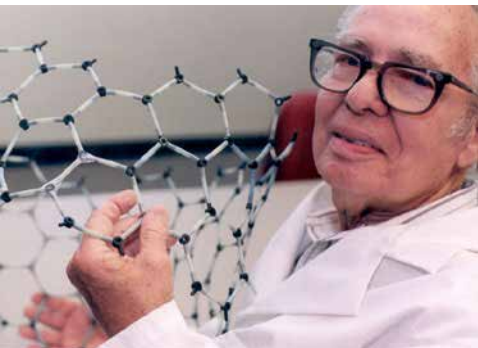
A major accomplishment involved the use of fluorine to cut nanotubes into ultra-short soluble single-walled carbon nanotubes (US SWNTS). Pyrolysis of the fluorinated tubes led to nanotubes as short as 50 nm. Researchers who use nanotubes for biological applications find this method to be the one of choice.

### **Chemistry for the people**

John's passion for chemistry was not limited to basic research. He loved bringing chemistry to all kinds of audiences. At Wisconsin-Madison he hosted an American Chemical Society-sponsored radio program that ran on a local station for a few minutes around noontime. The ACS provided some brief content for the program, and John added Wisconsin-specific material, such as information of interest to local farmers. He also hosted a television program that featured an on-air interview of a different science professor each program. Soon after his move to Rice, the campus radio station, KPRC, began featuring "Rice on TV" with John as the host, and this continued for several years.

Another manifestation of John's love of chemistry was his chemical magic show, which came to be entitled "Meaningful Manipulations of Millions of Madly Moving Molecules." This show originated as a presentation for his son David's sixth birthday and went on for thousands of performances by John or his trainees at local schools, libraries, shopping malls, and, especially, at the Houston Museum of Natural Science. For the museum, he not only did many presentations of the show himself, but he set up a system whereby classes of volunteer students trained their underclass successors so that the program's longevity was guaranteed. John also "donated" chemical magic shows as fundraisers for various charities. For a period, the American Chemical Society sponsored one show per year.

Besides the magic show connection, John served as a volunteer for the Houston Museum of Natural Science for many years. He was instrumental in putting together an appeal



**Margrave Manipulating Millions of Madly Moving Molecules.**

(Photo courtesy Rice University.)

for funding from the Robert A. Welch Foundation that led to the creation of the museum's Welch Hall of Chemistry. This exhibit currently logs the largest number of visitor hours of any exhibit in the museum, which is itself the third most frequently visited museum in the United States.

John was also a driving force in the establishment of the Houston Advanced Research Center (HARC), located in The Woodlands, a few miles north of Houston. This independent non-profit research entity was originally formed by a partnership of Rice, the University of Houston, and Texas A&M, a group that was later joined by the University of Texas at Austin. John served as

HARC's Vice President for Research and Chief Scientific Officer for several years. During this period he maintained full research laboratories on the Rice campus and at HARC, and travelled the 35 or so miles between the two locations almost daily.

In addition to his devotion to basic research, John always sustained a keen interest in applications of chemistry. He was an active consultant for national laboratories and several corporations, believing that it was a way to be in touch with the world into which most of his students and postdocs would spend their careers. Together with his student Richard Lagow, he founded a company known as Marchem, which primarily marketed products resulting from a "Marchem process" for coating objects with fluorine atoms.

Over the years John accumulated more than 30 U.S. and foreign patents. These were mainly related to the mainstream of his research, dealing with fluorine chemistry, chemical methods of preparing diamonds, or functionalization of fullerenes, for example. There are, however, a few surprises on the list, such as several patents for preservative and embalming fluids.

John was the founding editor of the international journal *High Temperature Science*, which began publication in 1969 in order to foster fundamental and practical uses of high-findings in this field. He continued as the journal's editor for many years. The journal changed its name to *High Temperature and Materials Science* in 1995, under which name it continued to be published through the end of 1997.

John was elected a member of the National Academy of Sciences in 1974. In addition to the three R&D100 Awards, his scientific research was recognized with several other honors: the American Chemical Society Award in Inorganic Chemistry (1967), the Southwest Regional ACS Award (1973), the Texas Institute of Chemists Honor Scroll Award (1978), the ACS Award in Fluorine Chemistry (1980), the Distinguished Alumnus Award of the University of Kansas (1981), the Sigma Xi Citation for Distinguished Scientific Achievement, and the Chemical Pioneer Award by the American Institute of Chemists (2003).

John was also a talented and devoted teacher of chemistry. His teaching portfolio included a sweeping range from freshman chemistry to advanced topics for graduate students. He brought the same enthusiasm and thoughtful scholarship to all of them. He regarded unglamorous assignments as challenges. At Wisconsin he enlivened a course for nursing students by making tea for the class and showing them the indicator properties of the brew. He was careful to put farming-related topics into his Wisconsin freshman chemistry classes. He was enough of a showman that his lectures were entertaining. He got the students to engage with chemistry—partially because of the intensity of his own passion for the subject. He often said that students who were faltering usually were not having trouble with the chemistry but with the mathematics.

Over the years, John had at least his fair share of brilliant and successful graduate students, some of whom he had recruited into chemistry. Richard Lagow is an interesting example. John talked him out of a football scholarship and into chemistry. Lagow went on to get a Ph.D. under John's direction and ended up as a full professor of chemistry at UT-Austin. At the other end of the spectrum, John had a special talent for rescuing faltering, unconfident grad students whom most of the other faculty had given up on. He would see the spark of ability in these lost sheep, fold them into his research laboratory, and help them transform themselves into winners.

John had a special devotion to graduate students and postdocs. His appointments as dean of advanced studies and research (1972-1980) and then vice president for advanced studies and research (1980-1986) at Rice attest to his concern for the well-being of the graduate student and postdoc populations. He and Mary Lou were among the organizers of a "loan closet" that provided access to household goods such as furniture and small appliances to successive generations of grad students and postdocs. And if there was heavy stuff to be moved, John was always ready for some lifting and hauling.

John also had enduring connections that originated with his army service. On mustering out of the Chemical Corps, he affiliated with the Army Reserve and remained an active member of that organization. He also acted for a number of years as the ROTC faculty advisor for Rice, and he met annually with Pentagon advisers planning ROTC curricula.

John was a renaissance chemist, as demonstrated by the diversity of projects that he undertook. No project was too big or challenging to be undertaken. Researchers will use the many innovations he developed for decades. His personal influence in the lives of his students and colleagues will long be remembered with respect and fondness.

### **ACKNOWLEDGEMENTS**

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